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# Density functional theory study of the magnetic moment of solute Mn in BCC Fe

D. J. M. King<sup>1\*</sup>, S. C. Middleburgh<sup>2,3</sup>, P. A. Burr<sup>4</sup>, T. M. Whiting<sup>1</sup>, P.C. Fossati<sup>1</sup>, M. R. Wenman<sup>1</sup>

<sup>1</sup>*Centre for Nuclear Engineering, Imperial College London, South Kensington, London, SW7 2AZ, United Kingdom*

<sup>2</sup>*Nuclear Futures Institute, Bangor University, Dean Street, Bangor, Wales, LL57 1UT, UK*

<sup>3</sup>*Westinghouse Electric Sweden AB, SE-721 63 Västerås, Sweden*

<sup>4</sup>*School of Electrical Engineering, University of New South Wales, Kensington, 2052, NSW, Australia*

*\*Corresponding Author:*

*E-mail: daniel.king@imperial.ac.uk*

*Telephone: +447474031955*

**Abstract.** An unexplained discrepancy exists between the experimentally measured and theoretically calculated magnetic moments of Mn in  $\alpha$ -Fe. In this study, we use density functional theory to suggest that this discrepancy is likely due to the local strain environment of a Mn atom in the Fe structure. The ferromagnetic coupling, found by experiment, was shown to be metastable and could be stabilised by a 2% hydrostatic compressive strain. The effects of Mn concentration, vacancies and interstitial defects on the magnetic moment of Mn are also discussed. It was found that the ground state, anti-ferromagnetic (AFM) coupling of Mn to Fe requires long range tensile relaxations of the neighbouring atoms along  $\langle 111 \rangle$  which is hindered in the presence of other Mn atoms. Vacancies and Fe interstitial defects stabilise the AFM coupling but are not expected to have a large effect on the average measured magnetic moment.

**Keywords:** density functional theory; ferrite; manganese; iron; RPV steels

## I. INTRODUCTION

Steels are ubiquitous in technological applications due to the abundance and low cost of Fe and its highly desirable mechanical and corrosion properties with alloying additions. Manganese is second only to C in its importance and use in steels. Historically, Mn has been included as both a minor and major alloying addition. The former to increase workability by suppressing FeS formation and latter to increase ductility, through twinning induced plasticity, in the fairly recently developed, so-called TWIP steels. The state-of-the art theoretical description of Mn in Fe has a large impact on our understanding of phenomena such as solute clustering<sup>1</sup> and vacancy-solute clustering<sup>2</sup>, which compromise the structural integrity of the steels during operation. The former occurs in the ferritic phase of duplex steels as a result of thermal ageing (573 – 773 K for >1000 h)<sup>3-5</sup> and in low-alloy steels<sup>6-8</sup> resulting from long-term (> 1 year) elevated temperature (~550 K); the latter, occurs due to neutron irradiation damage,

which is of interest to life extension of nuclear fission reactors and for fast neutron damage of steels to be used in future fusion reactors. It is therefore important for atomic scale processes such as binding, substitution and migration to be understood at a fundamental level, to be used in high order methods and analyses<sup>9–13</sup> to model these phenomena in industrial settings.

Mn has long been regarded as one of the most troublesome transition metals in terms of predicting its magnetic behaviour and electronic interaction with other elements<sup>14</sup>. In its elemental ground state, it adopts a 58 atom cubic unit cell of spacegroup  $I\bar{4}3m$ , and exhibits a non-collinear (NC) magnetic structure, whereby atoms located in 2a, 8c and two 24g sites (in Wyckoff notation) exhibit different spin vectors<sup>15,16</sup>. This magnetic structure undergoes a transition to paramagnetic (PM) structure at the Néel temperature of  $\sim 95$  K<sup>17</sup>. In contrast, Fe is one of the most well studied transition metals<sup>18–20</sup>. In its ground-state, Fe adopts a ferromagnetic (FM) BCC structure<sup>21</sup>, which it maintains until its Curie temperature at  $\sim 1043$  K<sup>22</sup>.

With minor alloying additions of Mn to Fe the crystal structure will remain BCC as a solid solution. The solubility limit is reached at  $\sim 3$  at. % at  $\sim 600$  K<sup>23</sup>, at equilibrium; however, increased additions are reported to be stabilised using cold working<sup>24</sup>. The magnetic structure of Fe-Mn alloys is highly variable and is thought to be affected by many different factors; namely, the Mn concentration<sup>25</sup>, the local atomic environment<sup>26</sup>, lattice parameter<sup>14</sup> and temperature<sup>24</sup>. This behaviour is observed to a much lesser extent for Fe-Cu, Fe-Ni and Fe-Si solid solutions<sup>27</sup>. It is therefore no surprise that discrepancies exist between experimental observations and theoretical frameworks. In the current study, we use density functional theory (DFT) to study the effect of concentration, local environment, strain and point defects on the magnetic moment and stability of Mn in  $\alpha$ -Fe.

## II. METHODOLOGY

A plane-wave density functional theory method was used, as implemented in the Vienna Ab initio Simulation Package (VASP)<sup>28</sup>. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional<sup>29</sup>, based on the Generalised Gradient Approximation (GGA), is used with the projector augmented wave (PAW) method<sup>30</sup>. Pseudopotentials provided with the VASP distribution were used, where 14 electrons ( $3p^6 3d^7 4s^1$ ) for Fe and 13 electrons ( $3p^6 3d^5 4s^2$ ) for Mn are considered as valence electrons.

The  $k$ -points, energy cut-off and lattice parameters the perfect lattice of both elements ( $\alpha$ -Fe and  $\alpha$ -Mn) were converged. It was determined that a real space  $k$ -point density of  $0.03 \text{ \AA}^{-3}$  and energy cut-off of 500 eV provided accurate results and were kept consistent for all calculations (resulting in  $6 \times 6 \times 6$ ,  $4 \times 4 \times 4$  and  $2 \times 2 \times 2$   $k$ -point grids for the 54, 128 and 250 atom supercells). Constant pressure, full relaxations with Methfessel-Paxton<sup>31</sup> smearing (with a width of 0.1 eV) were used to obtain the ground-state configurations. The tetrahedron smearing method with Blöchl corrections<sup>32</sup> was used on fixed dimension/volume calculations to generate the electronic density of states (DOS). Spin polarisation effects were also included; non-collinear and collinear theory was used for the  $\alpha$ -Mn structure. The electronic energy and ionic relaxation convergence criteria were set to  $10^{-6}$  and  $10^{-4}$  eV, respectively, for all calculations.

Supercells of 54 ( $3 \times 3 \times 3$ ), 128 ( $4 \times 4 \times 4$ ) and 250 ( $5 \times 5 \times 5$ ) Fe atoms were relaxed at constant pressure. To understand the behaviour of a dilute concentration of Mn in the  $\alpha$ -Fe lattice, a single Mn was substituted for an Fe atom in each of the supercell sizes. For higher concentrations of Mn and Mn-Mn interactions within the Fe matrix, a Mn content of 4.69 at. % was achieved by pseudo-randomly selecting six lattice sites for Mn atom substitution in the 128 atom supercell. As this method is stochastic in nature, this was repeated to produce 20 unique supercells (120 Mn atoms in total) to achieve a good statistical understanding of the system. Cohesive, binding, substitutional, vacancy and interstitial formation energies were calculated following standard procedures, outlined in the supplementary material.

Linear elastic theory, as implemented within the ANETO framework<sup>33</sup> for calculating the dipole tensor using the strain method<sup>34,35</sup>, was used calculate the relaxation volume and interaction energies for Mn in BCC ( $\alpha$ ) Fe in the.

### III. RESULTS AND DISCUSSION

#### A. Pure Mn and Fe

Table 1 reports the calculated values of cohesive enthalpies ( $E_c$ ) and lattice parameters ( $a_0$ ), presented for the ground-state ( $\alpha$ ), cubic ( $\beta$ ), FCC ( $\gamma$ ) and BCC ( $\delta$ ) Mn structures. Values for  $\alpha$ -Fe are

also provided, together with past literature values for Mn and Fe structures for comparison. The following magnetic structures within  $\alpha$ -Mn were considered: Non-magnetic (NM), collinear anti-ferromagnetic (AFM), non-collinear anti-ferromagnetic (NCL).

Table 1. Cohesive energy ( $E_c$ ) and lattice parameter ( $a_0$ ) of structural and magnetic allotropes of pure Mn and  $\alpha$ -Fe.

Crystal Structure	Magnetic Structure	$E_c$ (eV/atom)		$a_0$ (Å)	
		Current	Literature	Current	Literature
$\alpha$ -Mn	NCL	3.87	-	8.61	
	AFM	3.86	-	8.64	8.61 <sup>c</sup> , 8.91 <sup>d</sup>
	NM	3.82	-	8.56	
$\beta$ -Mn	AFM	3.79	-	6.32	6.32 <sup>e</sup>
$\gamma$ -Mn	NM	3.76	3.73 <sup>a</sup> , 2.92 <sup>b</sup>	3.50	3.49 <sup>f</sup>
$\delta$ -Mn	FM	3.69	-	2.79	2.78 <sup>g</sup>
$\alpha$ -Fe	FM	4.88	4.78 <sup>a</sup> , 4.28 <sup>b</sup>	2.83	2.86 <sup>b</sup>

References – theoretical: a<sup>36</sup>, c<sup>14</sup>, f<sup>37</sup>, g<sup>38</sup>; experimental: b<sup>39</sup>, d<sup>40</sup>, e<sup>41</sup>

In accordance with past literature, and the observed equilibrium behaviour of pure Mn, the  $\alpha$ -Mn phase is the most energetically favourable at 0 K<sup>42</sup>. This is then followed by  $\beta$ ,  $\gamma$  and  $\delta$  phases, which are temperature stabilised. The different known magnetic arrangements of  $\alpha$ -Mn were simulated, again predicting the behaviour as found in past literature<sup>14,16</sup>. The magnetic moments of each atomic site can be found in Table S1 (supplementary material). The overestimation of the cohesive enthalpies compared to the experimental values can be attributed to the approximation of the exchange-correlation functional<sup>36,43</sup>.

## B. Mn in $\alpha$ -Fe

### 1. Magnetic moment and stability

After gaining confidence in the theoretical representation of pure Fe and Mn, we move to the case in which a single Mn solute atom is placed in the  $\alpha$ -Fe matrix. The substitutional energy ( $E_{sub}$ ) provides an indication of the stability of Mn in the BCC FM Fe lattice. This value should converge with system size. Past literature has utilised 54 and 128 atom supercells where it was concluded that a convergence of  $\pm 0.05$  eV was achieved with the 128 atom supercell<sup>44</sup>. However, there is little agreement between the

magnetic moment of Mn and substitutional energy among theoretical literature<sup>27,44</sup>. In the publication by Olsson *et al.* 2010<sup>27</sup>, it was shown that the substitutional energy can vary  $\pm 0.3$  eV between the ultrasoft pseudopotential (USPP)<sup>45</sup> and PAW method and that there is a large discrepancy between the magnetic moment. This was attributed to the inability of the USPP method to correctly represent the semi-core  $d$  electrons. In this section we investigate the effect of magnetic moment of Mn on  $E_{\text{sub}}$ . It is known that the magnetic moment of Mn is particularly difficult to converge in  $\alpha$ -Fe as a shallow energy landscape exists between local FM and AFM states<sup>46</sup> (where all magnetic states are henceforth described, locally, in reference to the Fe matrix). Within this study it was found that the AFM state of Mn is the ground state in  $\alpha$ -Fe and that it is also possible to model the FM state in 128 and 250 atom supercells, provided a sufficiently high initial magnetic moment is set prior to energy minimisation, see Table 2. The average magnetic moment of Fe remained relatively consistent at  $2.26(1) \mu_B$  for all calculations within this section.

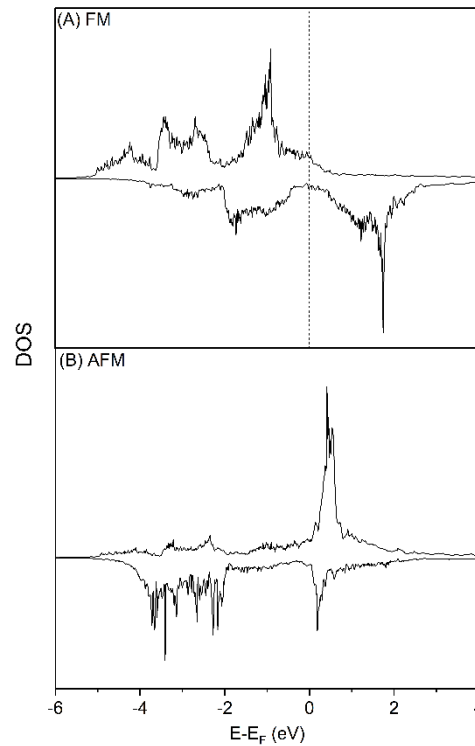
Table 2. Influence of initial spin on final spin state of Mn (relative to Fe) and the corresponding substitutional energies ( $E_{\text{sub}}$ ).

Supercell dimensions	Mn concentration (at. %)	Initial spin Mn ( $\mu_B$ )	Final spin Mn ( $\mu_B$ )	Final spin-state Mn	$E_{\text{sub}}$ (eV)
3×3×3	1.85	−2.00	−1.89	AFM	0.20
		0.00			
		2.00			
		4.00			
4×4×4	0.78	−2.00	−1.98	AFM	0.19
		0.00			
		2.00			
		4.00	0.54	FM	0.29
5×5×5	0.40	−2.00	−2.08	AFM	0.20
		0.00			
		2.00			
		4.00	0.74	FM	0.25

These results demonstrate that it is possible to converge to both the FM and AFM state of Mn when its initial magnetic moment is 4 or  $\leq 2$ , respectively, for supercell sizes  $\geq 128$  atoms. The corresponding

substitutional energies highlight the importance of the resultant magnetic moment of Mn to its stability in the  $\alpha$ -Fe matrix. When it is in the FM state the  $E_{sub}$  becomes less favourable by 0.10 eV and 0.05 eV for the  $4\times 4\times 4$  and  $5\times 5\times 5$  supercell, respectively. Since it is predicted that the AFM state is the more stable of the two, it is recommended that it is used as the reference state for the calculation of binding energy calculations.

When assessing the local density of states (LDOS) of Mn in  $\alpha$ -Fe, the FM and AFM spin-states are distinct, see Fig. 1. The difference in states is observed as the shift in the anti-bonding peak of the majority spin channel, from above the Fermi level for the AFM, to below the Fermi level in the FM magnetic coupling of Mn. The occupation of the anti-bonding peak explains the relative stability difference between the two states<sup>47</sup>.

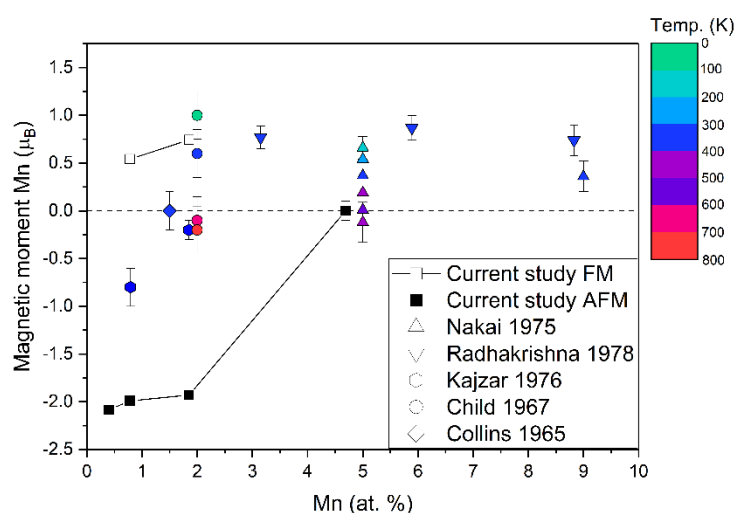


**Fig 1.** Local density of states of the d-band of (A) FM and (B) AFM spin coupling in  $\alpha$ -Fe for a 128 atom supercell.

## 2. Calculated vs experimental magnetic moment

In this section we compare the DFT calculated magnetic moments in the current study to the past experimental studies that used diffuse neutron scattering. For the former, the Mn concentration was varied by using the three different supercell sizes 250, 128 and 54 atoms correspond to 0.40, 0.78 and 1.85 at. %, respectively. A higher concentration of 4.69 at. % (above the expected solubility limit) was obtained by randomly populating the 128 atom supercell with 6 Mn atoms, repeated in 20 supercells; the average of all the magnetic moments were taken and the standard error is plotted as error bars.

Figure 2 shows that there is little agreement among the experimental data and that the ground state theoretical values, obtained in this work, over-predict the magnitude of the magnetic moment below 5 at. %. However, it should be emphasised that the solubility of Mn in  $\alpha$ -Fe is at maximum  $\sim 3$  at % at 600 K<sup>23</sup>. In the studies that surpass this solubility, Nakai *et al.*<sup>24</sup> reportedly stabilises the  $\alpha$ -phase by cold working and the study by Radhakrishna *et al.*<sup>26</sup> does not provide such information. Formation of secondary phases such as  $\gamma$ -(Mn,Fe) is likely to occur at equilibrium for Mn concentrations  $>3$  at. %. Nevertheless, the results in the current study are in better agreement with experimental findings for Mn in excess concentrations.



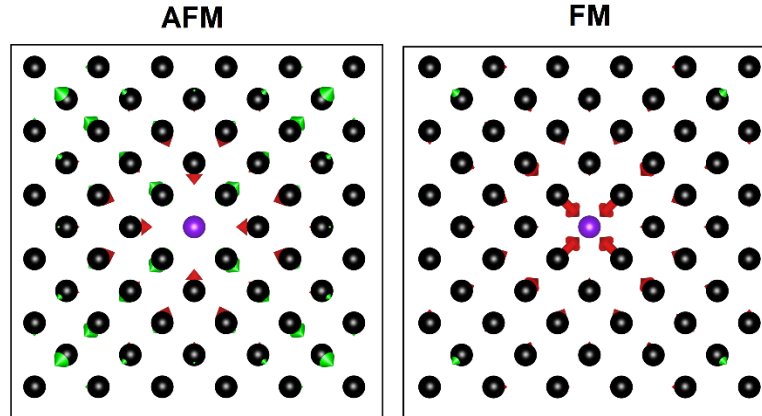
**Fig. 2.** Magnetic moment of Mn in  $\alpha$ -Fe as calculated using DFT in the current study for AFM Mn (closed squares) and FM Mn (open squares) compared to the experimental magnetic moments using diffuse neutron scattering, as measured by Nakai 1975 (coloured triangles), Radhakrishna 1978 (coloured inverted triangles), Kajzar 1976 (coloured hexagons), Child 1967 (coloured circles) and Collins 1965 (coloured diamonds) where the colours represent the temperature of the sample upon measurement.



In the following sections, the possible factors that lead to the discrepancies between experiment and theoretical calculations and how these differences can be captured through a mechanistic understanding of the Fe-Mn system are explored.

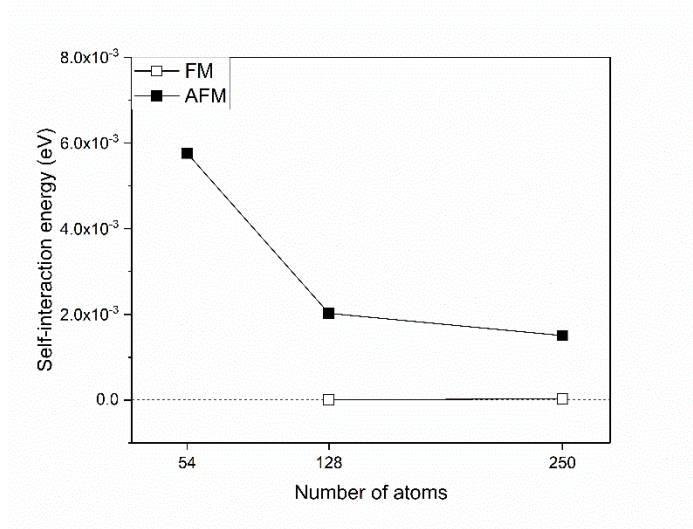
### 3. Atomic relaxations

By taking the difference between the atomic coordinates of the relaxed and unrelaxed supercells, the vectors corresponding to the atomic relaxations upon substitution of Fe with Mn can be calculated. Figure 3 provides an illustrative representation of the vectors ( $\times 100$ ) in a 250 atom supercell. Although these relaxations are small ( $\sim 10^{-2}$  Å) they are markedly different between FM and AFM states. For the AFM relaxation, the first nearest neighbour (1<sup>st</sup> nn) Fe was repelled by the Mn atom. The repulsion propagated along the  $\langle 111 \rangle$  over relatively long distances ( $\sim 10$  Å), while Fe atoms along the the  $\langle 100 \rangle$  and  $\langle 201 \rangle$  from the Mn experience a shorter-range attraction ( $\sim 5$  Å). In the FM case, only displacements of Fe towards Mn are observed (compressive), with the largest magnitude of  $1.3 \times 10^{-2}$  Å in the 1<sup>st</sup> nn Fe.



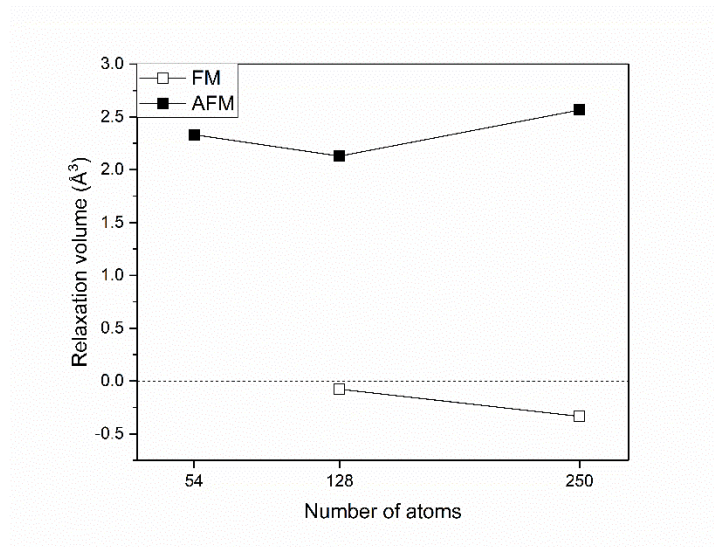
**Fig. 3.** Atomic relaxation vectors  $\times 100$  in compression (red) and tension (green) of Fe atoms around a Mn substitution (purple) for the AFM and FM magnetic moment of Mn in the 250 atom supercell.

For the smaller supercells (54 and 128 atoms) the long-range movement is more constrained and may explain the slight variance in magnetic moment and absence of FM moment for the 54 atom case. Figure 4 shows the elastic self-interaction energy<sup>48,49</sup>. It can be seen that the supercells are well converged by 128 atoms.



**Fig 4.** Self-interaction energy of the substitutional Mn defect in  $\alpha$ -Fe when in the FM and AFM magnetic state.

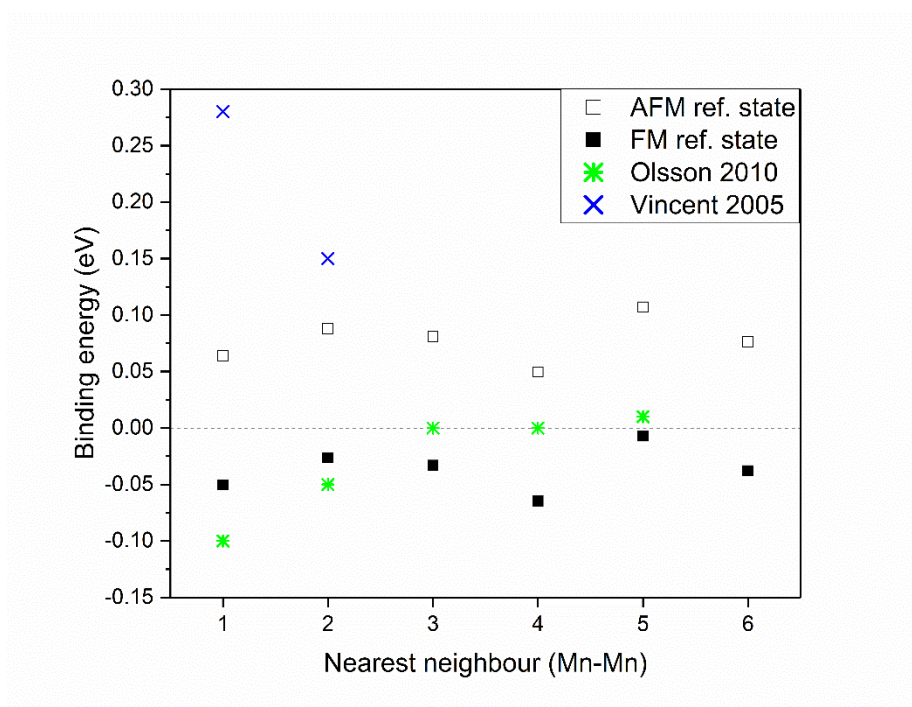
From linear elastic theory, the relaxation volumes of FM and AFM Mn are calculated for the different supercell sizes, see Fig. 5. The volume change due to the tensile relaxations of the AFM Mn and compressive relaxations of the FM Mn can be seen clearly. The effect of the FM Mn on the Fe lattice is much more localised than the AFM, where the former has self-interaction energies three orders of magnitude smaller than the latter. These results suggest that the increased stability of the AFM state over FM state of Mn is due to electronic rather than elastic effects.



**Fig 5.** Relaxation volume of the substitutional Mn defect in  $\alpha$ -Fe when in the FM and AFM magnetic state.

#### 4. Mn concentration

The interaction between neighbouring Mn species in  $\alpha$ -Fe is not well understood. Past theoretical studies that report the binding energies between two Mn atoms are not in accord<sup>27,44,50</sup>. Within this study, a stochastic behaviour was found in the resultant magnetic moments of the Mn. When two Mn atoms were placed in the 54, 128 and 250 atom supercells, in different nn positions, each adopted FM or AFM moments with varying magnitudes and no clear trend (reported in Figure S1 of the supplementary material). The binding energies between the two Mn atoms varied by  $\pm 0.05$  eV between supercells and did not correlate with their magnetic moment. Figure 6 reports the binding energies calculated for the 250 atom supercell, and provides a comparison with past literature. The calculation of the binding energy was done using the AFM and FM reference state, which results in a significant difference (0.14 eV) in energy.



**Fig. 6.** Mn-Mn nn binding energy for the 250 atom supercells using the AFM (open square) and FM (closed square) reference state. Comparison to Olsson (green star) and Vincent's (blue cross) work is included.

When comparing to the work of Olsson *et al.*<sup>27</sup>, the average binding energies calculated from the FM Mn in  $\alpha$ -Fe reference state are somewhat in agreement. However, the FM state is metastable therefore the AFM state should be taken as reference. This offset does not explain the discrepancy with

respect to the work of Vincent *et al.*<sup>44</sup>. It is more likely that the difference stems from the use of USPPs and other theoretical parameters.

When considering the difference in atomic relaxations for AFM and FM isolated Mn atoms, it is perhaps no surprise that there is a large variation in magnetic moment between nearest neighbour Mn with varying supercell size. If Mn does indeed prefer to exhibit AFM behaviour, then a more complex atomic relaxation is required. However, at certain geometries of nearest neighbour Mn and without sufficient long-range movement allowed, it will be more favourable for AFM and FM Mn atoms to coexist.

A more concentrated system, in which 6 Mn atoms are randomly distributed on a 128 atom BCC lattice replacing Fe, corresponding to a Mn concentration of 4.69 at. %, is now considered. Previous theoretical work on concentrated Fe-Mn systems conclude that there is a uniform switch from AFM to FM moment in Mn between 2 at % and 3 at. %<sup>51,52</sup>. In the current study, without sufficient statistical precision, this conclusion could mistakenly be made; of the 20 supercells studied, 15% displayed exclusively FM moments for Mn. However, the magnetic moment of Mn within the other 85% of the supercells were a mix of AFM and FM where the average moments across all supercells ranges from  $-0.8 \mu_B$  to  $0.9 \mu_B$ . Figure 7 shows the distribution of the magnetic moments of each Mn atom plotted against supercell energy. When taking the average of all 120 Mn atoms simulated, the magnetic moment equates to  $0.06 \mu_B$  (dotted line). The enthalpy of formation ( $E_{form}$ ) of the system displays a general trend whereby the systems with lower average magnetic moment (large dashes) are more energetically favourable. No correlation was found (correlation coefficient = 0.013) between the nearest neighbour species and the resultant magnetic moment of Mn, which vary between  $-2.2 \mu_B$  and  $1.1 \mu_B$ , see Fig. S2.

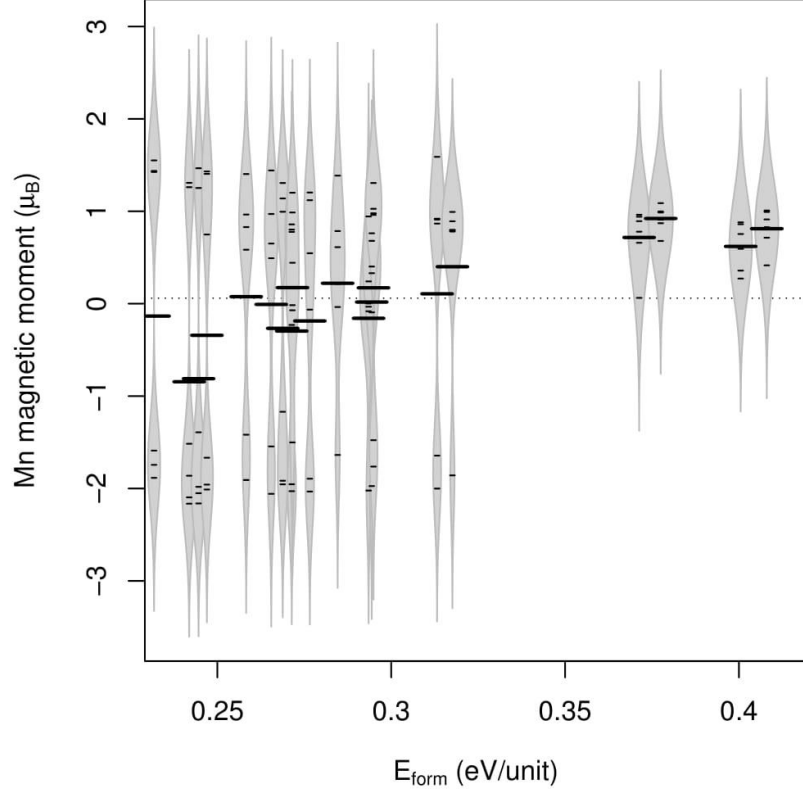


Figure 7. Magnetic moment of each Mn atom (small dashes), across the 20 supercells (grey shading), versus the enthalpy of formation per unit (3Mn:51Fe). The average magnetic moment per supercell and mean magnetic moment across all supercells is denoted by the large dashes and dotted line, respectively.

The environmental effect that is thought to influence the magnetic moment of  $\text{Mn}^{26}$  cannot be predicted by the nearest neighbour species or concentration of Mn in  $\alpha\text{-Fe}$ . Further, the presence of other Mn species does not stabilise a particular spin state. Rather, a more complex effect, likely due to the relaxation vectors around each Mn, is observed; resulting in an average moment close to zero (and median of  $\sim 0.70 \mu_B$ ). The interaction volumes used in diffuse neutron scattering vary greatly with experimental parameters<sup>53</sup>; it is expected that these volumes are of the  $\mu\text{m}$  length scale (although not explicitly stated) in references from Section III(B)(2). Therefore, the overall average magnetic moment is an important result for comparison to literature.

### 5. Effect of strain

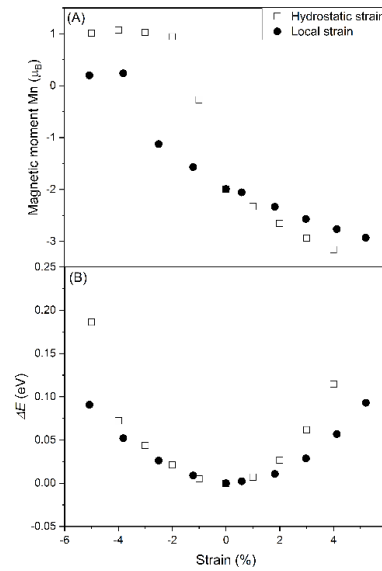
In the past, it has been demonstrated that the lattice parameter of  $\alpha\text{-Mn}$  has a large effect on its magnetic structure<sup>14</sup>. To-date this effect has not been investigated in the Fe-Mn system, however pioneering work by Cable *et al.* has explored this effect in Ni- and Co- Mn alloys<sup>54</sup>. Two methods of

straining the environment around the Mn atom were used in this study, both using 128 atom supercells: Applying tension and compression (1) hydrostatically and fixing the volume and shape of the supercell while allowing internal relaxation of the atoms and (2) locally in the 1<sup>st</sup> nn Fe, fixing supercell shape and atomic positions of atoms. The latter performed to investigate the influence of only the 1<sup>st</sup> nn.

At the dilute limit, the effect of strain on the magnetic moment of Mn is clear; compression (negative strain) induces the FM moment and tension induces the AFM moment, see Fig. 8(A). The results from the hydrostatic method show a transition from AFM to FM moment between 0 and –2% strain. For the locally strained case, the transition occurs at higher compressive strains and to a lesser degree. This discrepancy is considered to be the result of the influence of the neighbouring atoms, other than the 1<sup>st</sup> nn, which remain fixed. The difference in internal energy is calculated as:

$$\Delta E = \frac{E_{strained} - E_{gs}}{n_d} \quad (1)$$

where  $E_{strained}$  and  $E_{gs}$  are the total internal energy of the strained and ground state supercell, respectively, normalised to the number of displaced atoms ( $n_d$ ). The results follow the expected parabolic distribution where deviation from the ground state configuration leads to less favourable energies (Fig. 8(B)).

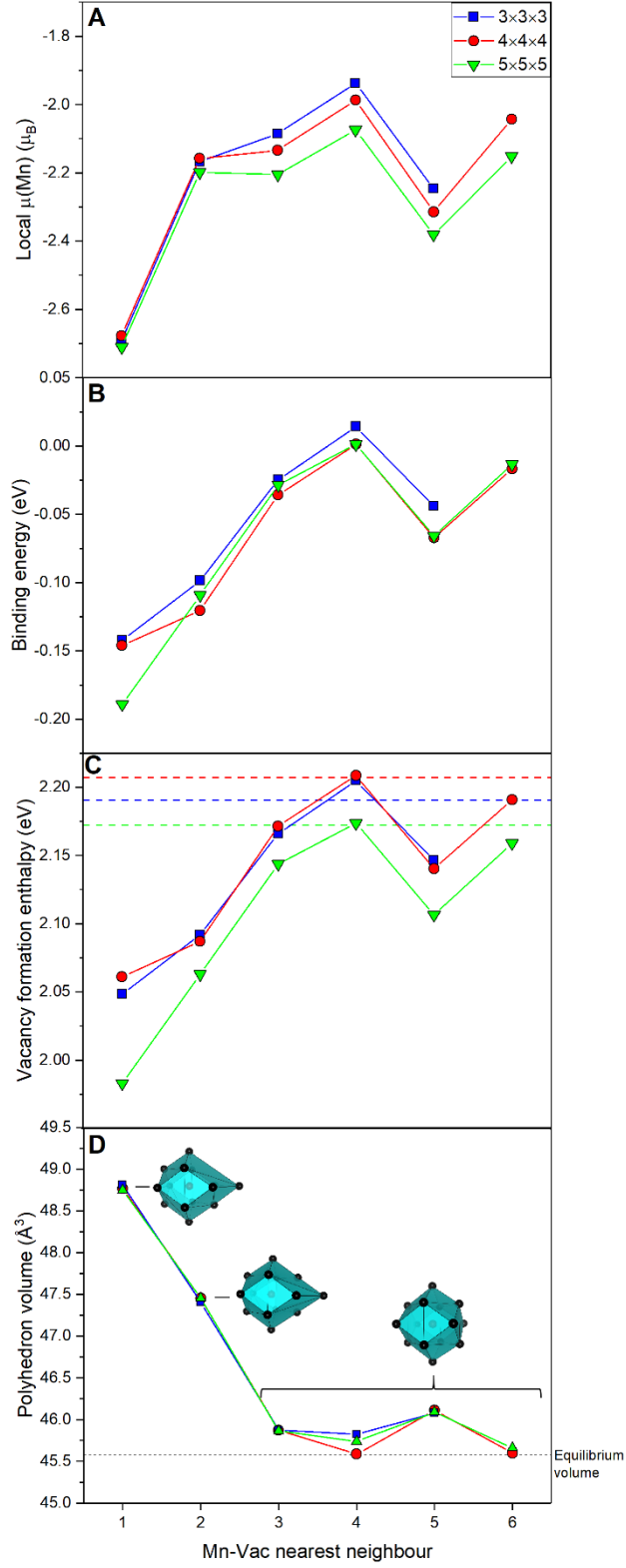


**Fig. 8.** Magnetic moment of Mn (A) and difference in internal energy of strained and ground-state supercell,  $\Delta E$ , normalised by the number of strained atoms (B) with a comparison between hydrostatic strain (open squares) and local 1<sup>st</sup> nn strain (closed circles).

These results suggest that the disagreement between observed experimental magnetic moment of Mn is likely due to the different conditions of the samples. Non-equilibrium features such as increased defect concentrations and residual stress, due to quenching or cold-working, are expected to have a large impact on the measured magnetic moment of Mn in Fe. A lattice parameter change of 0.03 Å equates to a strain of 1%. Experimentally, an increase in temperature of ~250 K leads to lattice parameter increase of 0.01 Å for  $\alpha$ -Fe<sup>55</sup>. Without considering phonon interactions and other temperature effects, it is postulated that it is entirely possible to observe both AFM and FM average moments in samples with the same concentration of Mn providing the temperature is varied sufficiently or is under sufficient elastic strain, as seen by Child *et al.*<sup>56</sup> and Nakai *et al.*<sup>24</sup>. However, caution must be used when making direct comparisons to experiment. This is because the approximation of the exchange-correlation functional used by DFT introduces discrepancies to both the lattice parameter and magnitude of magnetic moment<sup>57</sup>. Therefore, this result should be taken qualitatively and an experimental relation between strain and magnetic moment is required to establish a quantitative relationship.

### ***6. Effect of vacancies***

Vacancies are ubiquitous in crystalline systems and vary in concentration depending on the condition and processing of the sample<sup>58</sup>. Vacancy-solute clusters are a documented phenomenon<sup>59,60</sup> and the binding of solute atoms to vacancies in  $\alpha$ -Fe is important for understanding solute partitioning, diffusivity and precipitation<sup>61–63</sup>. In Figure 9(A-C), the resultant magnetic moment, binding energy and vacancy formation energy of Mn substitution are shown as a function of distance from a vacancy from 1<sup>st</sup> – 6<sup>th</sup> nn.



**Fig. 9.** (A) Mn local magnetic moment, (B) Mn-vac binding energy and (C) vacancy formation enthalpy in the  $\alpha$ -Fe matrix for 1<sup>st</sup> – 6<sup>th</sup> nn for a 3×3×3 (blue square), 4×4×4 (red circle) and 5×5×5 (green triangle) dimension supercell, dashed lines with the same colours in panel (C) represent the vacancy formation enthalpies of pure Fe. (D) The volumes of the polyhedron created by the 1<sup>st</sup> and 2<sup>nd</sup> nn around the Mn solute atom. When the Mn was in 1<sup>st</sup> and 2<sup>nd</sup> nn proximity to the vacancy the polyhedron was extended to the 3<sup>rd</sup> nn in that direction (pictorial representations). The equilibrium volume for a single Mn in the  $\alpha$ -Fe matrix is provided for reference (dashed line).



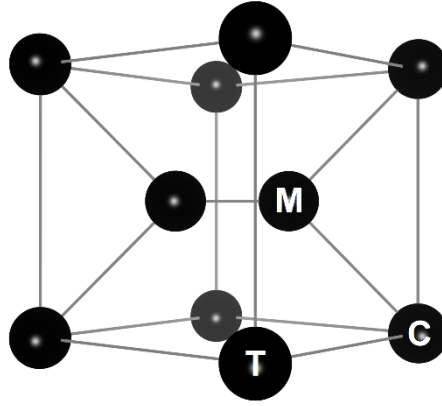
The magnitudes and trend of the binding energies are in accordance with past theoretical findings<sup>27,44,64</sup>. It is predicted that it is favourable for Mn to bind to an Fe vacancy, with a relatively long-range attraction compared to other 3d transitional metals<sup>27,65,66</sup>. There is a clear stabilisation of the AFM moment of Mn when in the 1<sup>st</sup> nn position and the binding energy between Mn and vacancy follows a similar trend of the magnetic moment for all supercell sizes. This behaviour is different to many of the other transition metals, which show little variance in magnetic moment with vacancy position<sup>27</sup>. The vacancy formation enthalpies ( $E_{vac}$ ) follow the same trends seen in the magnetic moment and binding energies. Compared to pure Fe, there is a significant lowering in  $E_{vac}$  in the 1<sup>st</sup> and 2<sup>nd</sup> nn to the Mn. Again, it must be emphasised that, when calculating the binding energy, the use of the metastable FM Mn reference state in  $\alpha$ -Fe leads to a difference in binding energy of 0.06 eV (more favourable) to the ground-state AFM reference state.

The non-linear trend in binding energies is interesting especially because it is expected that the binding energy should tend to zero with increasing distance. Here, it is found that the Friedel-like perturbations of the Fe around the vacancy dominate over those around the Mn substitution. By assessing the volume of the polyhedron created by the 1<sup>st</sup> and 2<sup>nd</sup> nn around the Mn atom, a negative correlation to the binding energies and magnetic moment is found, see Fig. 9(D). When Mn is in the 1<sup>st</sup> and 2<sup>nd</sup> nn (to the vacancy) the polyhedron is extended to the 3<sup>rd</sup> nn (from Mn) in the direction of the absent site. These findings follow the trend identified within this study *i.e.* the FM moment is stabilised by compressive and AFM by tensile lattice strain. At equilibrium, without a vacancy, the 2<sup>nd</sup> nn polyhedron volume containing Mn is calculated to be 45.60 Å<sup>3</sup>, which corresponds to the ground-state magnetic moment of  $-2 \mu_B$ . When only using 1<sup>st</sup> nn polyhedron volumes no correlation was found.

From an applied perspective the equilibrium vacancy concentration is quite small in Fe  $\leq 10^{-6}$  below the melting temperature<sup>2,67</sup>. However, when subject to displacive radiation damage these concentrations can become non-trivial. It is possible that the increased stability when Mn is under local tensile strain, in the presence of a vacancy, is the basis for solute-vacancy stabilisation seen experimentally<sup>2</sup> or hypothesised to occur due to nucleation of solutes from defects in RPV steels<sup>6</sup>.

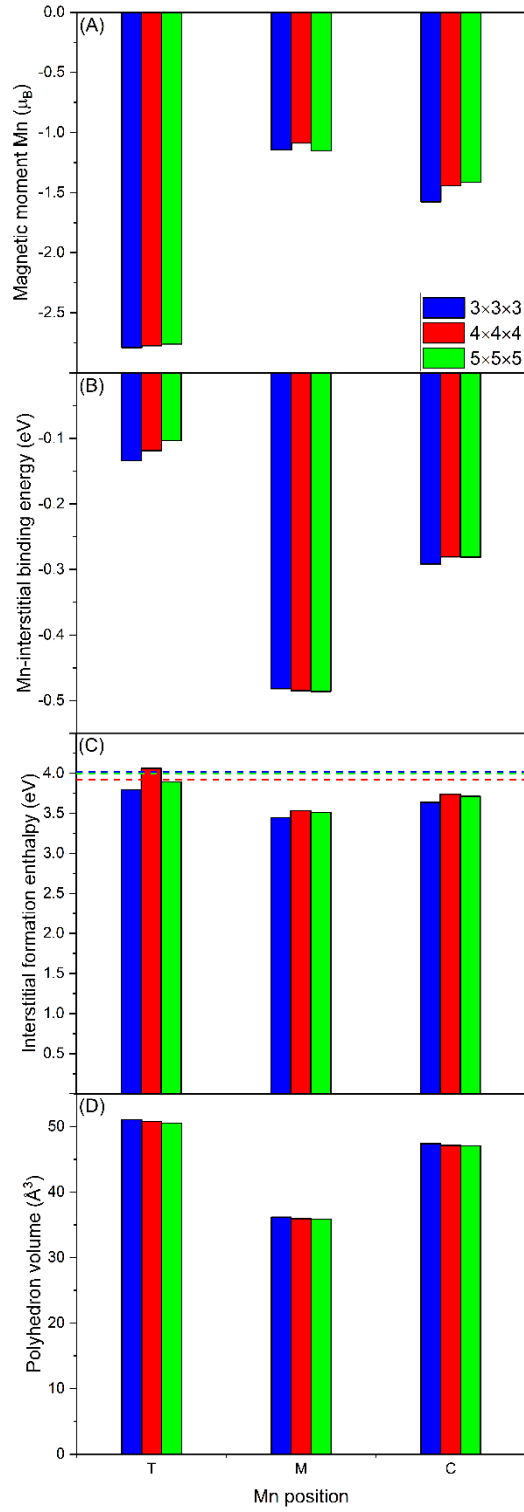
### 7. Effect of the $\langle 110 \rangle$ Fe interstitial

Unlike the majority of BCC metals, the most stable self-interstitial configuration in  $\alpha$ -Fe is the  $\langle 110 \rangle$  dumbbell<sup>68</sup>. Although Mn has been shown to also have a strong binding to the  $\langle 111 \rangle$  Fe dumbbell interstitial, it is expected that the  $\langle 110 \rangle$  will be the most prevalent interstitial in  $\alpha$ -Fe<sup>27</sup>. For this reason, only the  $\langle 110 \rangle$  orientation was considered with Mn at three positions around the Fe interstitial: Mixed (M), Compressive (C) and Tensile (T), see Fig. 10. Within this study these denotations are arbitrary, however, to remain consistent to past literature where the names are given in reference to their respective Voronoi polyhedra volumes<sup>12</sup>, we continue their use. From our current work, it is identified that the 2<sup>nd</sup> nn displacement has a non-negligible effect on the magnetic moment of Mn (Section B(5)), therefore a Voronoi analysis is not expected to correlate with the resultant magnetic moment of Mn.



**Fig. 10.**  $\langle 110 \rangle$  interstitial dumbbell configuration in  $\alpha$ -Fe. Labels M (mixed), C (compressed), and T (tensile) denote the position of the Mn substitution with respect to a dumbbell.

In agreement with past work, the binding energies between Mn and an Fe  $\langle 110 \rangle$  interstitial were favourable in all three sites, see Fig. 11. A difference in binding energy between FM and AFM Mn reference state was found to be 0.08 and 0.06 eV for  $4 \times 4 \times 4$  and  $5 \times 5 \times 5$  supercells, respectively. Interestingly, the relative magnetic moments do not follow the same trend as seen with the vacancy defects. Analysis of the 2<sup>nd</sup> nn polyhedra volumes again display a negative correlation with the magnetic moments, as seen with the vacancies.



**Fig. 11.** (A) Mn local magnetic moment, (B) binding energy and (C)  $\langle 110 \rangle$  interstitial formation enthalpy in the  $\alpha$ -Fe matrix for T, M and C sites for a 3 $\times$ 3 $\times$ 3 (blue), 4 $\times$ 4 $\times$ 4 (red) and 5 $\times$ 5 $\times$ 5 (green) dimension supercell, dashed lines with the same colours in panel (C) represent the interstitial formation energies of pure Fe. (D) The volumes of the polyhedron created by the 1<sup>st</sup> and 2<sup>nd</sup> nn around the Mn solute atom.

In the absence of Mn, the magnetic moment of the two Fe atoms in the  $\langle 110 \rangle$  dumbbell configuration, exhibit a weak AFM coupling to the matrix  $-0.27(2) \mu_B$ . Further, the 1<sup>st</sup> nn Fe atoms to the dumbbell display a significant deviation in magnitude of their magnetic moment from the matrix. The 4 Fe atoms in the geometrically equivalent C and T sites yield magnetic moments of  $\sim 1.72(7)$  and  $\sim 2.42(1) \mu_B$ , respectively, which vary only slightly with Mn substitution. It is likely that the introduction of a self-interstitial atom sufficiently changes the atomic and magnetic structure so that the magnitudes of the 2<sup>nd</sup> nn polyhedron volume vs magnetic moment relationship, determined for the undefective and vacated cases, no longer holds true. Nevertheless, the coupling of Mn to Fe is consistently AFM.

#### IV. CONCLUSIONS

- The discrepancy in magnetic moment of Mn in  $\alpha$ -Fe, that exists between theory and experiment, is likely due to susceptibility of the magnetic moment to change with strain. Here, it was found that a hydrostatic compressive strain of  $-2\%$  ( $0.06 \text{ \AA}$ ) stabilised the FM state of Mn atoms (relative to Fe). Strains imposed by quenching, cold working or thermal expansion are expected to dominate over the effect due to Mn concentration, vacancies and Fe interstitial atoms. Therefore, it is extremely important to provide experimental details pertaining to the lattice parameter and sample conditions in future assessment of the magnetic moment of Mn in Fe.
- In the dilute case, it is possible to simulate both FM and AFM states of Mn, where the former is metastable, by initialising the spin state on Mn to 4 and  $\leq 2 \mu_B$ , respectively. The relaxations of the Fe atoms around the FM and AFM Mn differ significantly. A long range tensile relaxation in the  $\langle 111 \rangle$  and compression in the  $\langle 100 \rangle$  and  $\langle 201 \rangle$  occur for the AFM case and strictly compressive relaxations for the FM. The AFM state is the ground state for dilute Mn defects in  $\alpha$ -Fe should be used as a reference state to calculate the binding energies of defect complexes in future work.
- At higher Mn concentrations, Mn exhibits AFM and FM spin states in a stochastic manner with an average moment of  $\sim 0.06 \mu_B$  and median of  $\sim 0.70 \mu_B$ . By providing a statistically significant dataset, we show that the previous theory of a uniform switch from AFM to FM between

2 – 3 at. % Mn, is an artefact of inadequate statistical sampling. This randomness is likely due to a combination of shallow energy landscape between AFM and FM spin-states and the inability for relaxations of the surrounding atoms to occur for specific geometries and concentrations of Mn, as to allow for exclusively one state to exist.

- A vacancy and  $\langle 110 \rangle$  Fe interstitial were both found to stabilise the AFM moment of Mn. The atomic relaxations due to the defects dominate over those around the Mn substitution. Polyhedron analysis of the atoms within the 2<sup>nd</sup> nn to Mn show a negative correlation between volume and magnetic moment with varying nn distance to the vacancy/interstitial. This result suggests that the relationship between magnetic moment and local strain still exists when in the presence of a vacancy or interstitial.

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